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DOI:
10.1016/j.polymertesting.2013.05.012

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Document Version
Peer reviewed version

Citation for published version (Harvard):
Xin, H, Shepherd, D & Dearn, KD 2013, 'Strength of poly-ether-ether-ketone : effects of sterilisation and thermal ageing', *Polymer Testing*, vol. 32, no. 6, pp. 1001-1005. https://doi.org/10.1016/j.polymertesting.2013.05.012

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DOI 10.1016/j.polymertesting.2013.05.012

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Strength of poly-ether-ether-ketone: effects of sterilisation and thermal ageing

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Author generated final version. Published as:

Xin H, Shepherd DET & Dearn KD (2013). Strength of polyether-ether-ketone: effects of sterilisation and thermal ageing. *Polymer Testing* 32: 1001-1005.

Abstract

This paper investigates the strength of polyether-ether-ketone (PEEK) after sterilisation and thermal ageing. PEEK specimens were divided into five groups, according to whether the specimens had been annealed, sterilised or aged. Specimens were subjected to either static or dynamic three-point bend tests. Static tests involved loading the specimens until a maximum displacement of 40 mm was reached. Dynamic tests involved applying a sinusoidally varying force at a frequency of 5 Hz. The maximum force applied to a specimen was based on a percentage of the static yield strength. Testing continued until failure or run out of 10 million cycles. Sterilisation and ageing resulted in no significant change in the static yield strength. Annealing was found to significantly increase the yield strength. For the dynamic tests, the fatigue strength was in the range 99.4 to 107.4 MPa; sterilisation and thermal ageing were found to have no effect on fatigue strength.

Keywords: Fatigue strength; Flexural strength; Gamma sterilisation; Poly-ether-ether-ketone (PEEK); Thermal ageing.

1. Introduction

PEEK (poly-ether-ether-ketone) is a semi-crystal high performance thermoplastic of the poly-aryl family[1-2]. Its inherent linear polymer chain conforms to a resonance stable arrangement, where the ether and ketone functional groups locate at the opposite end of the benzene rings[2]. This unique chemical structure leads to its high thermal stability and high mechanical performance. PEEK exhibits a high glass transition temperature (T_g) of 143°C and a high melting temperature (T_m) of 343°C [1,3]. Unreinforced PEEK 450G has a Young's modulus of 3.7 GPa and a flexural yielding strength of 165 MPa, shows virtually no anisotropy and has a tan colour[4,5].

The initial clinical application of PEEK was in the Brantigan lumbar intervetebral body fusion cage (Depuy Spine, Rayaham, MA)[6]. Since this, PEEK or carbon reinforced PEEK have been extensively used in a range of implants such as total joint replacment (Epoch hip stem by Zimmer Inc., Warsaw, IN), disc arthroplasty bearing surfaces (NuBac® Lumbar intra-disc and NuNec® Cervical disc arthroplasties by Pioneer Surgical Technology Inc., Driebergen, Netherlands) and internal fracture fixation plates (Piccolo plating system by CarboFix Orthopedics Inc., Herzeliya, Israel)[7-9].

A detailed understanding of the static and fatigue performance of PEEK is essential for its use in medical implant design. Several studies[10-20] have presented fatigue data on PEEK and its composite; however, none have investigated the effects of ageing and sterilisation. The aim of this study was to investigate the effects of gamma-irradiated sterilisation and thermal ageing on the static and fatigue strength of unreinforced PEEK.

2. Materials and Methods

2.1 PEEK specimens

The PEEK specimens were prepared from unreinforced PEEK 450G (Victrex Plc., Lancashire, UK) in sheet form, with a nominal thickness of 6 mm. The tolerances on the sheet thickness were + 0.2 mm to + 0.7 mm. These sheets were cut using a band saw (1 mm blade thickness) into rectangular specimens with 140 mm length x 15 mm width, according to ISO 178: 2003. Prior to testing, the exact dimensions of each specimen were measured using a digital calliper (Fisher Scientific Ltd., UK) with 0.01 mm precision, at three different locations along the length of each specimen.

The specimens were then divided into five groups, according to whether the specimens had been annealed, sterilised or aged (Table 1). Annealing treatment was conducted in a Cabolite PN30 oven (Scientific Laboratory Supplies Ltd., Orchard house, Hessle, East Riding of Yorkshire, UK) with gravity convection, at 250°C for a minimum of four hours[21]. Sterilisation was achieved using gamma-irradiation, in a dosage range of 25-40 kGy by Isotron Ltd. (Morary Road, Elgin Industrial Estate, Swindon, UK). Specimens that were aged were placed in a Cabolite PN30 oven, at 90°C for either 96 days or 192 days[10]. These times for ageing correspond to roughly 10 and 20 years, respectively, *in-vivo* ageing based on the 10 degree empirical rule[22,23].

2.2 Static tests

Specimens were subjected to a three-point bend test according to ISO 178 [24], using a Lloyd 6000R materials testing machine (Lloyd Instruments Ltd., West Sussex, UK), operated using Windap V1.6 software (LIoyd Instruments Ltd., West Sussex, UK). An aluminium test rig was designed and manufactured, as shown in Fig. 1. The lower test rig consisted of two supports (112 mm apart) that attached to the base of the testing machine. The PEEK specimen was placed on the supports. The upper test rig, which was attached to the actuator of the testing machine, consisted of a bar with a 5 mm radius at the end. The actuator of the materials testing machine was set to lower at a rate of 0.033 mm/s[24]. Load and displacement were recorded throughout the tests. Testing continued until a maximum displacement of 40 mm had been applied. Graphs of load against displacement were plotted. Seven specimens from each of the five groups in Table 1 were tested.

From the graphs of load against displacement, the peak load (i.e. maximum sustained load) was considered as the yielding load (F) and its corresponding displacement was defined as the yielding displacement (δ). Subsequently, the flexural strength (σ) was calculated according to Eq. 1 [24])

$$\sigma = \frac{3Fl}{2bd^2} \qquad (1)$$

where l is the span length, b is the width, and d is the thickness.

2.3 Dynamic tests

All fatigue tests were performed with the same three-point bending test rig, as described for the static tests (section 2.2). For dynamic tests a Bose 3300 materials testing machine (Bose Corporation, ElectroForce Systems Group, Minnesota, USA) was used, controlled by Win test software. Testing involved applying a sinusoidally varying force at a frequency of 5 Hz, at room temperature. The ratio of maximum to minimum force was 10. The maximum force applied to a specimen was based on a percentage (60-85%) of the static yield strength of group 3 specimens, determined in section 2.2. Ten or eleven PEEK specimens from groups 3, 4 and 5 (Table 1) were subjected to the dynamic tests. Testing continued until fracture of a specimen or run out of 10 million cycles. Graphs of stress against number of cycles to failure (i.e. stress-life) were plotted on a log scale, and the corresponding gradients and intercepts were determined via linear regression analysis.

2.4 SEM

Fractured PEEK surfaces were analysed using a Philips XL-30 FEG environmental scanning electron microscope (SEM) with Oxford Inca EDS system (FEI Company, Hillsboro, USA). The specimens were initially prepared by cutting the fractured sample into a rectangular block (5 × 15 × 7 mm) and then sputter coating with a thin layer of gold using a Polaron E5000 sputter-coating unit (Polaron Ltd., London, UK). Subsequently, the SEM scans were taken at 5 kV acceleration voltage. The failure mechanisms were then interpreted from the SEM fracto-graphy images.

2.5 Statistical analysis

The statistical analysis was performed using Sigmaplot Version 11.0 (Systat Software Inc., London, UK). One way ANOVA plus Tukey pair-wise multiple comparisons were adopted to compare the results among different groups. Statistical analysis of the regression coefficients of the stress-life graph was performed according to the method of Cohen[25]. Moreover, a pooled variance was used to obtain the standard error for each regression coefficient, due to the lower number of data points. The significance level was set at $p<0.05$ for all statistical analysis.

3. Results

3.1 Static tests

A typical load-displacement graph of a PEEK specimen is shown in Fig. 2. It initially displays a linear trend. After reaching the yielding point, the PEEK specimen begins to soften with a declining load, until the displacement limit is reached. The obtained yielding loads and yielding displacements are shown in Table 2. ANOVA analysis shows that the yield strength among the annealed groups (group 2 to 5) are not significantly different ($p \geq 0.44$, for each two groups), while the strength of group 1 is significantly smaller than group 2 ($p < 0.001$).

3.2 Dynamic tests

The plotted stress-life curves from the dynamic tests are shown in Fig. 3. It can be seen that the number of cycles to failure increases with decreasing stress for each of the groups. The recorded flexural fatigue strengths (i.e. the stress corresponding to 10 million cycle survival) were 97.4 MPa (for group 4) and 107.4 MPa (for group 3 and group 5). The average fatigue strength is 104.1 ± 5.8 MPa among all groups. The gradients and intercepts of the regression fitted lines are shown in Table 3. ANOVA analysis of the regression coefficients shows that there is no significant difference between the regression lines.

3.3 SEM results

The SEM fracto-graphy images from the fatigue tests were used to determine the general fracture mechanisms. Figs 4 and 5 show the main fracture pattern which includes three consecutive regions of crack initiation (Fig 5b) , a parabolic propagation region and a fast fracture zone. From Fig. 5a, it reveals that the large parabolic feature propagates along the fracture direction, combined with other encountered parabolic features, until it reaches the fast fracture zone. It is worth mentioning that fine striations (Fig. 5c) were observed in front of the parabolic features.

4. Discussion

The flexural yield strengths of the annealed groups are comparable to the manufacturer's reported value of 165 MPa[4]. Among groups 2 to 5, the statistical analysis shows that there are no significant changes in yielding strength after either gamma sterilisation or thermal aging, or both ($p \geq 0.44$). This finding is consistent with other studies. Cartwright and Devine [26] reported that 200 kGy gamma irradiation followed by extended ASTM F2003-02[27] accelerated ageing (70°C and in 5bar Oxygen pressure, for 40 days) did not lead to any significant yield strength deterioration of PEEK 450G extruded rod. The results of this study show that annealing resulted in an obvious enhancement of yield strength (groups 1 vs. 2, $p < 0.001$). This phenomenon can be explained as a gain in material crystallinity, which has been reported previously[28]. As PEEK is a two-phase material, its mechanical strength is dominated by its crystal phase, therefore a higher crystallinity will lead to a higher mechanical strength[29].

The effects of sterilisation and thermal ageing on polymers are commonly manifested by the formation of an oxidation layer, discolouration and embrittlement[30]. Understanding these characteristics is crucial for determining the operational longevity and structural safety of medical implants[31]. For the inherent aromatic stable structure of PEEK, it is expected to withstand a dose level of well over 10^4 kGy of gamma irradiation without a significant degradation of properties[30]. This superior irradiation resistance can be explained by short-life free radicals (i.e. high energy contained unstable species) that were generated during the sterilisation process[32]. Up to now, there is no standard procedure for accelerated ageing of PEEK. Several authors[26,33] adopted the ASTM F2003-02 [27] practise, which is for Ultra High Molecule Weight Polyethylene and uses elevated temperature and oxygen pressure.

To determine the total fatigue lifetime change after sterilisation and thermal ageing, a simple Augest wöhler stress-life fatigue approach [11,16] was used rather than the advanced crack propagation method [15], due to its relative simplicity. The recorded flexural fatigue strengths were varied in the range of 97.4 MPa to 107.4 MPa. Regression coefficients analysis shows that the stress-life curves (Fig. 3) were not statistically different to each other. This means that sterilisation, thermal ageing, or both do not induce any obvious change in fatigue performance; the fatigue strengths of the groups can be considered as from a single population. Mean fatigue strength of 104.1 ± 5.8 MPa was obtained for all the fatigue specimens. It roughly accounts for 63% of the reported flexural yielding strength of PEEK 450G.

It has been proposed that the fatigue property of PEEK is depended on both the intrinsic material attributes and extrinsic testing conditions[15]. Caution should be taken for adopting these fatigue data in actual implant design with different operation or testing conditions. For example, fatigue testing of PEEK based spinal discs should be conducted in a 0.9% saline environmental bath at 37^{o}C, under a testing rate of 2 Hz or less[34]. Moreover, the tensile fatigue strength of PEEK 450G with a crystallinity value of 22.5% was previously reported as 58.72 MPa at one million cycles, which is much lower than the fatigue results obtained in this study[11,16]. In addition, it is worth noting that PEEK is a notch weakening material [15], thus design related weaknesses or material defects should be taken into account during the design of actual medical devices.

The observed fracture patterns were consistent with other studies [35] where, fracture initiates as void nucleation at the inclusion/flaws (as shown in Fig. 5b), leads to the formation of large parabolic feature, until it reaches fast fracture region. The fine fatigue striations (Fig. 5c) have also been seen in other PEEK fatigue studies[15,18] and indicate for the individual cycle of crack growth.

5. Conclusions

In this study, the effects of sterilisation and thermal ageing on the static and fatigue flexural strengths of PEEK 450G were investigated. For static flexural strength, the effects of sterilization combined with thermal ageing are negligible. In contrast, annealing treatment results in a significant enhancement in flexural strength. The fatigue strength is in the range of 99.4 to 107.4 MPa. Sterilisation and thermal ageing did not lead to any obvious change in fatigue performance.

Acknowledgements

The authors would like to thank Mr Carl T. Hingley for the help of preparing the raw specimen. Victrex PLC is thanked for providing the PEEK 450G plate. Funding for the testing machine was from the Arthritis Research Campaign (now Arthritis Research UK).

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Tables

Table 1. Pre-treatments and subsequent static and dynamic test methods for all specimens.

Group No.	Annealing	Sterilisation	Thermal ageing	No. of specimens	Test method
1	No	No	No	7	Static
2	Yes	No	No	7	Static
3	Yes	Yes	No	7	Static
				10	Dynamic
4	Yes	Yes	90°C, 96 days	7	Static
				11	Dynamic
5	Yes	Yes	90°C,192 days	7	Static
				10	Dynamic

Table 2. Load at yield, deflection at yield and flexural strength for the static tests on the five groups of specimens. All values mean ± standard deviation

Group No.	1	2	3	4	5
Load at yield (N)	611.5 ± 28.4	731.3 ± 33.7	721.3 ± 34.8	749.7 ± 25.0	741.8 ± 31.6
Deflection at yield (mm)	20.2 ± 1.0	22.5 ± 1.6	21.1 ± 1.0	21.00 ± 0.6	21.0 ± 1.1
Flexural strength (MPa)	139.8 ± 6.5	167.2 ± 7.7	164.88 ± 7.9	171.36 ± 5.7	169.6 ± 7.2

Table 3. Coefficients of regression

Group No.	Gradient	Intercept	R^2
3	-8.4	162.7	0.78
4	-12.2	178.9	0.94
5	-8.6	170.6	0.58

Figures

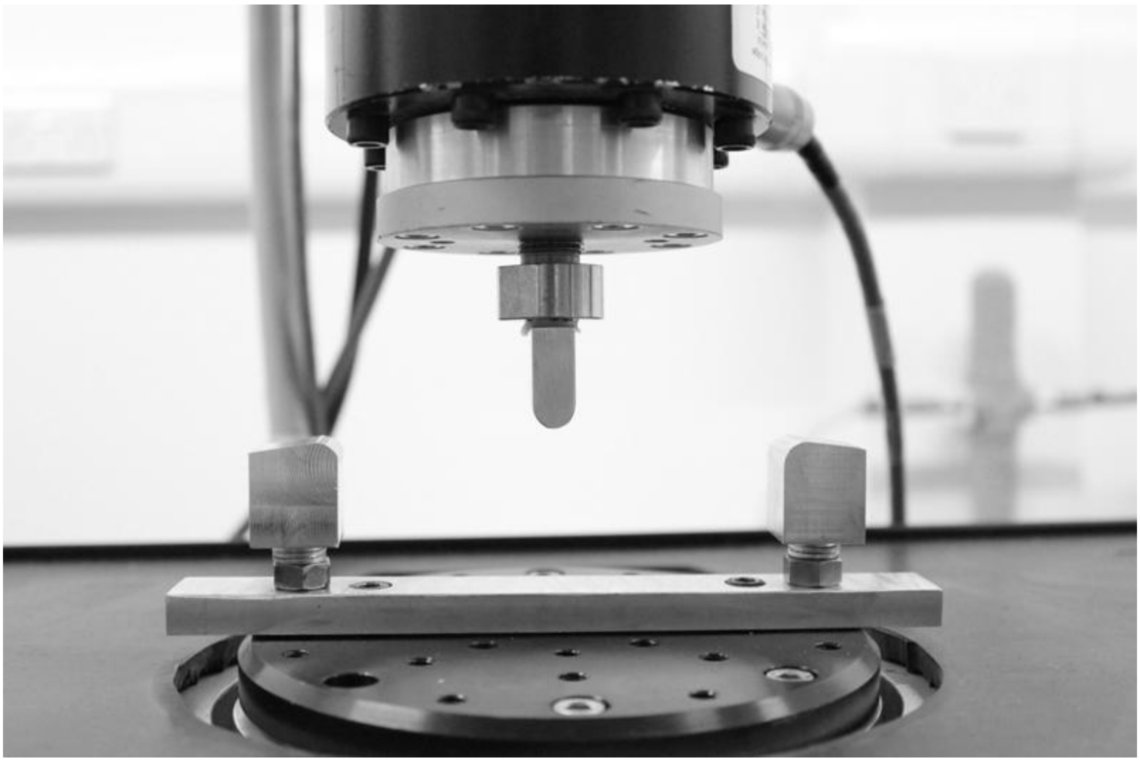

Fig 1. Three-point bend test rig.

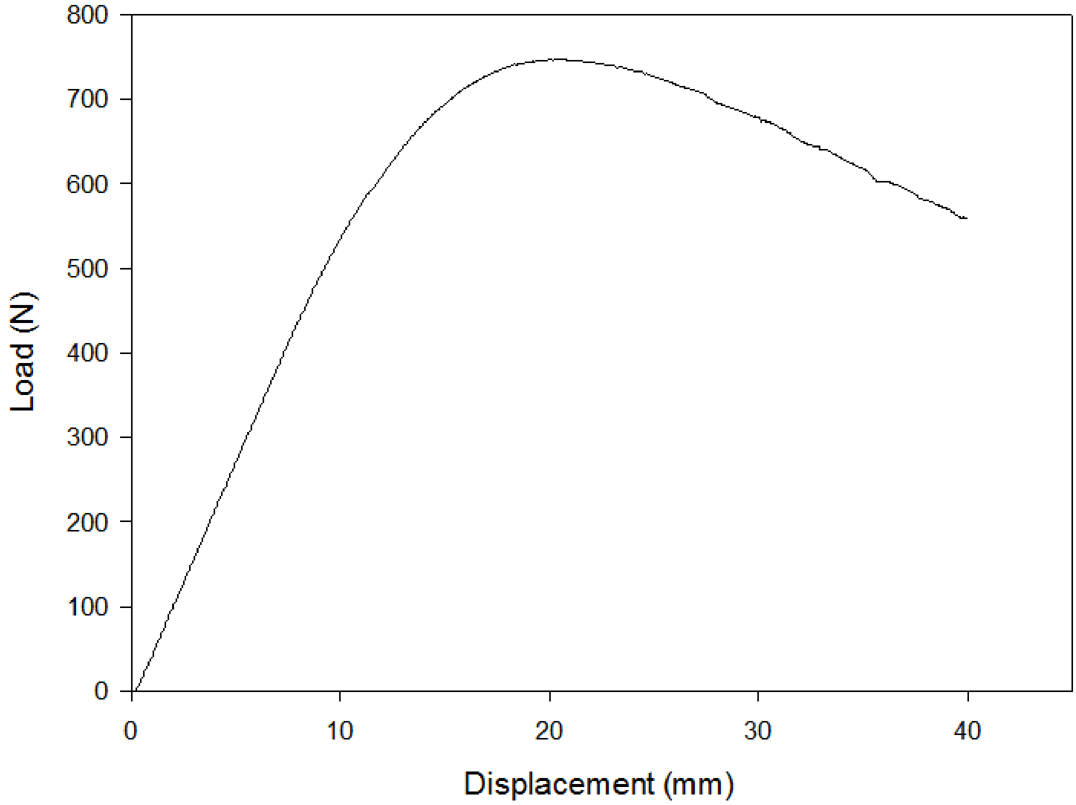

Fig. 2. Graph of load against displacement for Group 3, specimen 2.

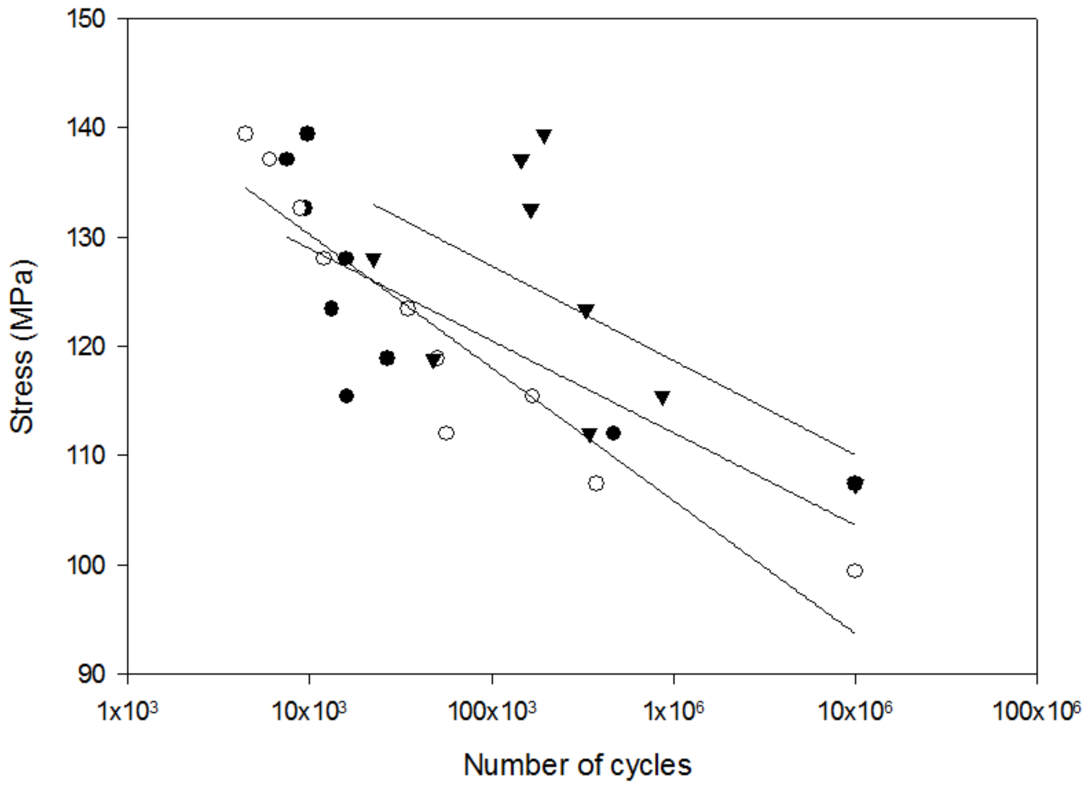

Fig. 3. Stress against number of cycles to failure (or run out); x-axis is on a logarithmic scale, base 10. ● group 3; ○ group 4; ▼ group 5.

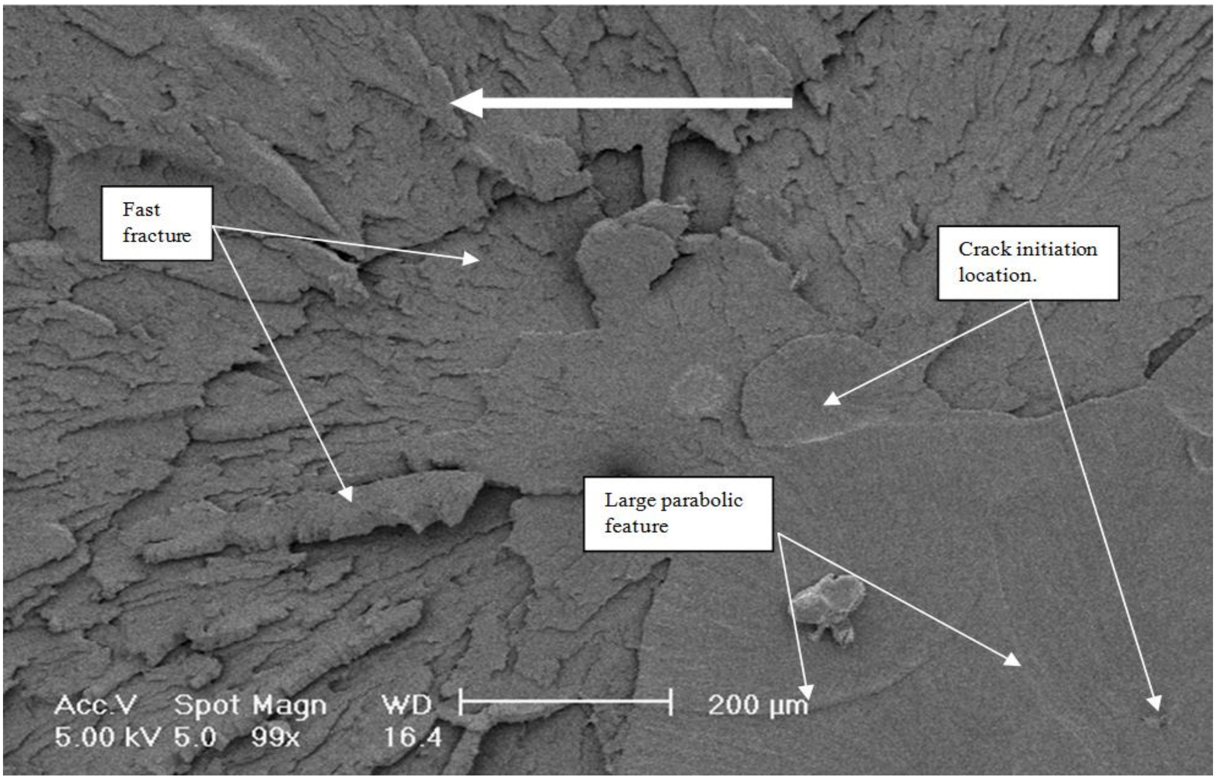

Fig. 4. SEM fracto-graph for Group 3 dynamic, specimen 10. The fracture direction is from right to left.

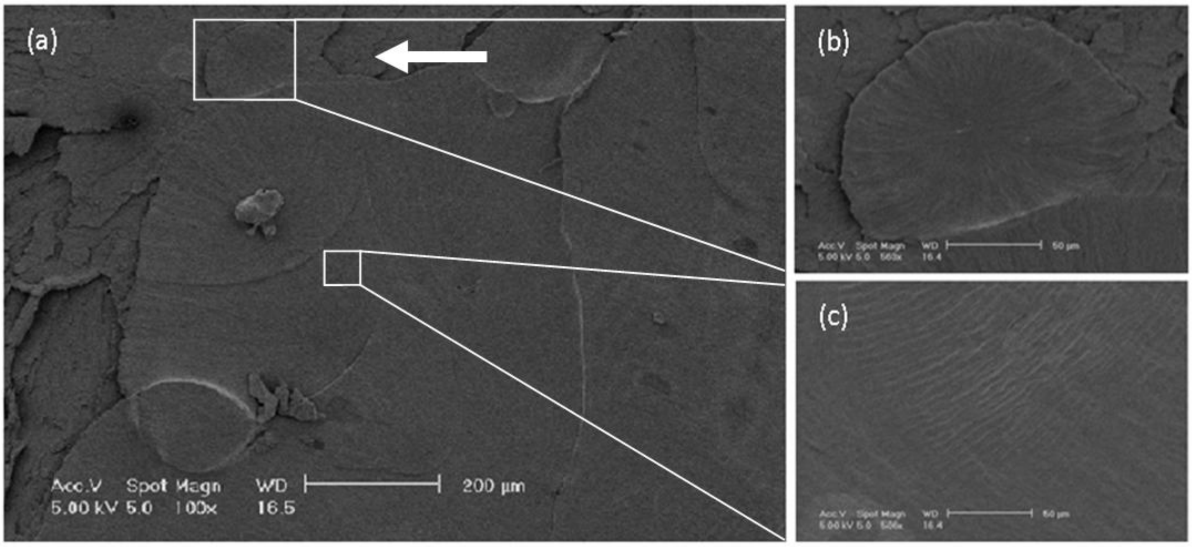

Fig. 5. Enlarged Fig. 4. a) parabolic fracture feature; b) Void nucleation site; c) Fine fatigue striation.